

Algorithms for Computing Matrix Elements by Green's Function Monte Carlo

Peter J. Reynolds

Office of Naval Research

NATO Advanced Study Institute
on Monte Carlo Methods in
Physics and Chemistry

Cornell University

July 12-25, 1998

Outline

Diagonal

- Second-order estimators
- Sampling the ratio Ψ_0 / Ψ_T
 - auxiliary walks
 - tagging to keep track of offspring
- Correlated sampling
- Carrying weights before branching

Off-Diagonal

- Second-order estimators
- Messy “exact” approaches

The Problem(s)

- Usual QMC averages are “mixed expectation values” $\langle \Psi_T | A | \Psi_0 \rangle$
- If $[A, H] \neq 0$ (e.g. dipole, quadrupole moments, V , derivative operators, etc.)

$$\langle \Psi_T | A | \Psi_0 \rangle \neq \langle \Psi_0 | A | \Psi_0 \rangle$$

(normalization hidden)

- How to compute $\langle \Psi_m | A | \Psi_n \rangle$ elements

Second-order Estimator

Mixed average is accurate to “first order” in

$\delta \equiv \Psi_0 - \Psi_T$...terms like $\langle \Psi_0 | \delta \rangle$ and $\langle \Psi_0 | A | \delta \rangle$

Trial expectation $\langle \Psi_T | A | \Psi_T \rangle$ also 1st order δ

Combining first-order estimators

$$\begin{aligned} A^{(2)} &= 2 \langle \Psi_0 | A | \Psi_T \rangle - \langle \Psi_T | A | \Psi_T \rangle \\ &= \langle \Psi_0 | A | \Psi_0 \rangle + O(\delta^2) \end{aligned}$$

Advantage: low statistical error, especially if computed “differentially”

Weighting with Ψ_0 / Ψ_T

- Use weight to convert from mixed to

$$\frac{\langle A(\Psi_0 / \Psi_T) \rangle_f^{\text{pure}}}{\langle (\Psi_0 / \Psi_T) \rangle_f} = \frac{\langle \Psi_T | A(\Psi_0 / \Psi_T) | \Psi_0 \rangle}{\langle \Psi_T | (\Psi_0 / \Psi_T) | \Psi_0 \rangle} \frac{\langle \Psi_T | \Psi_0 \rangle}{\langle \Psi_T | \Psi_0 \rangle} = \frac{\langle \Psi_0 | A | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

- How get $\Psi_0(\mathbf{R})/\Psi_T(\mathbf{R})$?

- *Answer:* Asymptotic number of descendants from QMC walk which starts at **R**

K. S. Liu, M. H. Kalos, and G. V. Chester, Phys. Rev. A **10**, 303 (1974)

$\Psi_0(\mathbf{R})/\Psi_T(\mathbf{R})$ “Forward-walking” of Kalos et al.

- Initial distribution given by a single walk

$$f_R(\mathbf{R}') = \Psi_T(\mathbf{R}') \psi(\mathbf{R}', t=0) = \delta(\mathbf{R}' - \mathbf{R})$$

- Expanding ψ in complete set of eigenfun

$$\delta(\mathbf{R}' - \mathbf{R}) = \Psi_T(\mathbf{R}') \sum_j c_j \varphi_j(\mathbf{R}')$$

- c_j : multiply by $\varphi_i(\mathbf{R}')/\Psi_T(\mathbf{R}')$;

$$\text{integrate over } (\mathbf{R}') / \Psi_T(\mathbf{R})$$

Asymptotic population

- Asymptotically distribution

$$P(\mathbf{R}) = c_0 \exp\{t(E_0 - E_R)\} \Psi_0(\mathbf{R}) \Psi_T(\mathbf{R})$$

- Substitute c_0 ; integrate over all space
count descendants; find asymptotic pop
resulting from walker starting at $\mathbf{R}$:

$$\begin{aligned} P(\mathbf{R}) &= \int \Psi_0(\mathbf{R}') / \Psi_T(\mathbf{R}') \exp\{t(E_0 - E_R)\} \Psi_0(\mathbf{R}) \Psi_T(\mathbf{R}') d\mathbf{R}' \\ &= \Psi_0(\mathbf{R}) / \Psi_T(\mathbf{R}) \exp\{t(E_0 - E_R)\} \langle \Psi_T | \Psi_0 \rangle \end{aligned}$$

$P(\mathbf{R})$ used in both numerator and denominator for
expectation values

... final factors cancel

Implementations

- QMC walk with auxiliary (side) walks (what you'd expect from previous discussion)
- VMC walk with pairs of side walks
- Single QMC walk with “tagging” to track family tree

Implementations

- QMC walk with auxiliary (side) walks (what you'd expect from previous discussion)
- *VMC walk with pairs of side walks*
- Single QMC walk with “tagging” to track family tree

VMC with QMC side walks

- VMC walks are very efficient; can employ large time steps; have no τ bias.
- Points from VMC are initial points for QMC side walks to obtain P .
- Since walkers distributed as Ψ_T^2 , need $|\Psi_0 / \Psi_T|^2$ to obtain pure expectation values.
- Two *independent* samplings because P^2 not unbiased estimate of $|\Psi_0 / \Psi_T|^2$ despite $\langle P \rangle = \Psi_0 / \Psi_T$.
- Sampling A and two estimates of P gives trial, mixed, *and* pure expectation values.

Correlated VMC with QMC side walks

- VMC + QMC side walks: error in $(A_T - A_p)$ generally much smaller than that of A_p alone, since A_p and A_T are correlated.
- Useful because A_T can be quickly computed in separate VMC to high precision.

Implementations

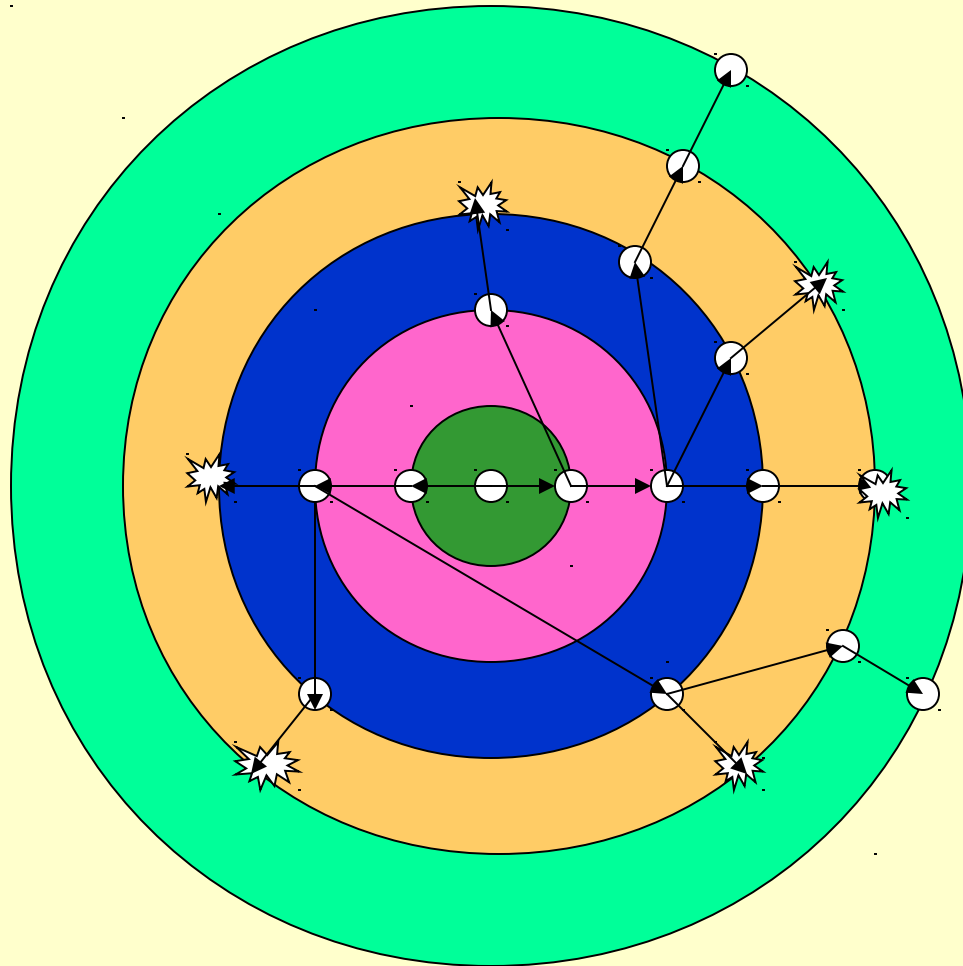
- QMC walk with auxiliary (side) walks (what you'd expect from previous discussion)
- VMC walk with pairs of side walks
- *Single QMC walk with “tagging” to track family tree*

R.N. Barnett, P.J. Reynolds, W.A. Lester, Jr., J. Comp. Phys **96**, 258 (1991)

Tagging algorithm

- Avoids start-up cost of equilibrating each side walk N steps to get $P(\mathbf{R})$
- Use a single (branching) walk and find N -distant offspring of each generation
- Construct a family tree as walk progresses
- Each walker is labeled so that its location in the tree is specified. Requires two tags.

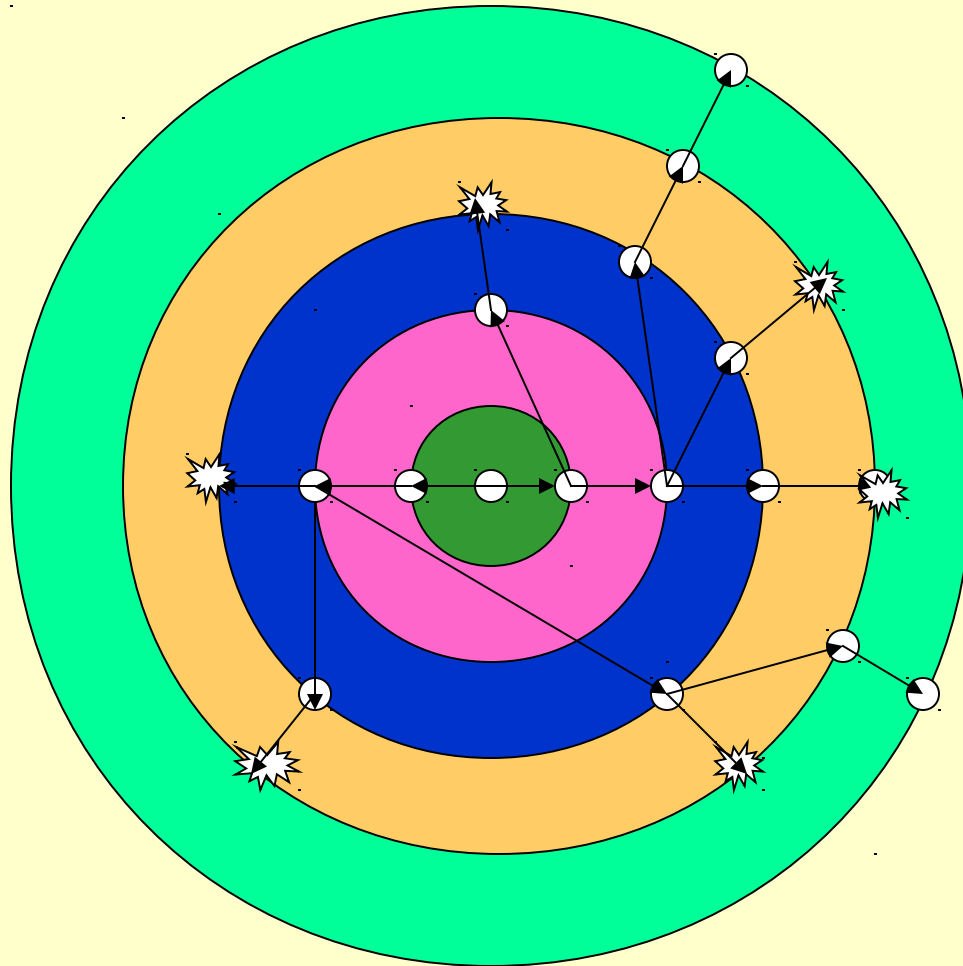
Tagging diagram



Tagging

- $0 \leq \theta \leq \Theta$ gives (with t) walker's location in the tree [unique angular and radial point in diagram]
- δ specifies range within tree in which descendants of this walker can be placed
- Offspring get sub-ranges $\varepsilon [\theta, \theta + \delta]$. Makes identification of progeny possible for entire future (descendant spaces never overlap)
- Enables determination of convergence in a single calculation.

Tagging diagram



Branching with weighting

- Omit integer rounding until weight becomes exceedingly small or large.
- Then integer weight and branch—but assign daughters weights of I_w / w , rather than unity, so no loss of information occurs.
- Decreases variance

Off-diagonal Matrix elements?

- Transition dipole moment

$$\mathbf{r}_{mn} = \langle \Psi_m | \sum_i \mathbf{r}_i | \Psi_n \rangle$$

- Experimental observables

» Oscillator strength

$$f_{mn} = \frac{2}{3} (E_n - E_m) |\mathbf{r}_{mn}|^2$$

» Excited-state lifetimes

$$\tau_n = \frac{3}{2} g_n / (g_m f_{mn} \bar{\nu}^2)$$

Second-order Estimator

- Can we do something similar to $A^{(2)}$?

- Define $A_{\tau\tau} = \langle \Psi_{Tm} | A | \Psi_{Tn} \rangle$

$$A_{m\tau} = \langle \Psi_m | A | \Psi_{Tn} \rangle$$

$$A_{n\tau} = \langle \Psi_{Tm} | A | \Psi_n \rangle$$

- $A^{(2)}_{mn} = A_{m\tau} + A_{n\tau} - A_{\tau\tau}$

□ error $O(\langle \delta_m | A | \delta_n \rangle)$

- Need off-diagonal mixed/trial

Off-diagonal mixed/trial elements by Re-weighting

- $A_{\tau\tau} = \langle \Psi_{Tm} | A | \Psi_{Tn} \rangle$

Sample $\Psi_{Tm} A \Psi_{Tn} / |\Psi_T|^2$ from $|\Psi_T|^2$ (VMC)

- $A_{m\tau} = \langle \Psi_m | A | \Psi_{Tn} \rangle$

Sample $A \Psi_{Tn} / \Psi_{Tm}$ from $\Psi_{Tm} \Psi_m$ (mixed: QMC)

» *Note: all wave functions assumed normalized*

Exact off-diagonal elements

Approaches

- QMC sampling with QMC side walks for weights
 - QMC sampling with Green's function expectation values as weights
 - VMC sampling with QMC side walks for weights
-
- R.N. Barnett, P.J. Reynolds, W.A. Lester, Jr., J. Chem. Phys. **96**, 2141 (1992)

Exact off-diagonal elements

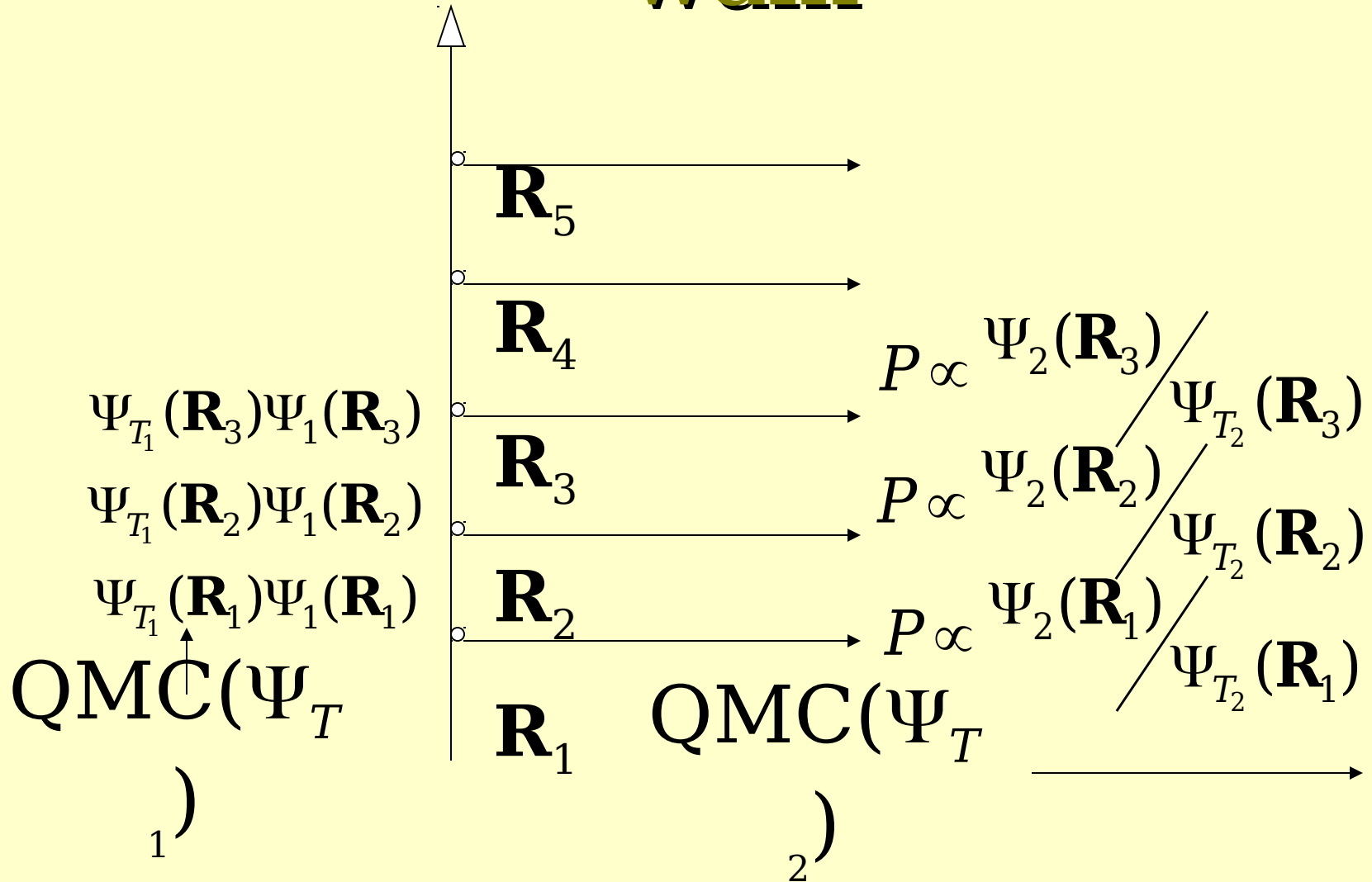
Approaches

- *QMC sampling with QMC side walks for weights*
 - QMC sampling with Green's function expectation values as weights
 - VMC sampling with QMC side walks for weights
-
- R.N. Barnett, P.J. Reynolds, W.A. Lester, Jr., J. Chem. Phys. **96**, 2141 (1992)

Exact off-diagonal elements (QMC sampling)

- Goal $\langle O \rangle_{f_1} \equiv \frac{\langle \Psi_{T_1} | O | \Psi_1 \rangle}{\langle \Psi_{T_1} | \Psi_1 \rangle} = \langle \Psi_1 | A | \Psi_2 \rangle$
- Need $O = s_1 \Psi_2(\mathbf{R}) \Psi_{T_1}^{-1}(\mathbf{R}) A(\mathbf{R})$
with $s_i \equiv \langle \Psi_{T_i} | \Psi_i \rangle$
- For $\Psi_2(\mathbf{R})$ use $P_2(\mathbf{R})$

QMC walks within QMC walk



Exact off-diagonal elements (QMC sampling)

- Now

$$O = s_1 s_2^{-1} w(t) \Psi_{T_2}(\mathbf{R}) \Psi_{T_1}^{-1}(\mathbf{R}) P_2(\mathbf{R}, t) A(\mathbf{R})$$

with

$$w(t) \equiv \exp[(E_2 - E_{R_2})t]$$

- s_i and $w(t)$ still need to be determined
- $w(t)$ from monitoring population growth

$$w(t) = \frac{\langle P_2(\mathbf{R}, t + \Delta t) \rangle_{f_1}}{\langle P_2(\mathbf{R}, t) \rangle_{f_1}}^{t/\Delta t}$$

Exact off-diagonal elements (QMC sampling)

- Now

$$O = s_1 s_2^{-1} w(t) \Psi_{T_2}(\mathbf{R}) \Psi_{T_1}^{-1}(\mathbf{R}) P_2(\mathbf{R}, t) A(\mathbf{R})$$

with $w(t) \equiv \exp[-(E_2 - E_{R_2})t]$

- s_i and $w(t)$ still need to be determined
- s_i from

$$\langle P_i(\mathbf{R}, t) \rangle_{|\Psi_{T_i}|} = s_i^2 w_i(-t)$$

Exact off-diagonal elements

Approaches

- QMC sampling with QMC side walks for weights
 - *QMC sampling with Green's function expectation values as weights*
 - VMC sampling with QMC side walks for weights
-
- R.N. Barnett, P.J. Reynolds, W.A. Lester, Jr., J. Chem. Phys. **96**, 2141 (1992)

Exact off-diagonal elements

(Green's function averaging)

$$\begin{aligned}
 \langle G(\mathbf{R}', \tau) \rangle_{f_1} &\equiv \frac{\int G(\mathbf{R} \rightarrow \mathbf{R}', \tau) f_i(\mathbf{R}, t) d\mathbf{R}}{\int f_i(\mathbf{R}, t) d\mathbf{R}} \\
 &= f_i(\mathbf{R}, t + \tau) / \int f_i(\mathbf{R}, t) d\mathbf{R} \\
 &\xrightarrow{t \rightarrow \infty} \exp[-\tau(E_i - E_{R_i})] \Psi_{T_i}(\mathbf{R}') \Psi_i(\mathbf{R}) s_i^{-1} \\
 &= w_i(\tau) \Psi_{T_i}(\mathbf{R}') \Psi_i(\mathbf{R}) s_i^{-1}
 \end{aligned}$$

An alternative forward walk to generate $\Psi_i(\mathbf{R})$

Exact off-diagonal elements

(Green's function averaging)

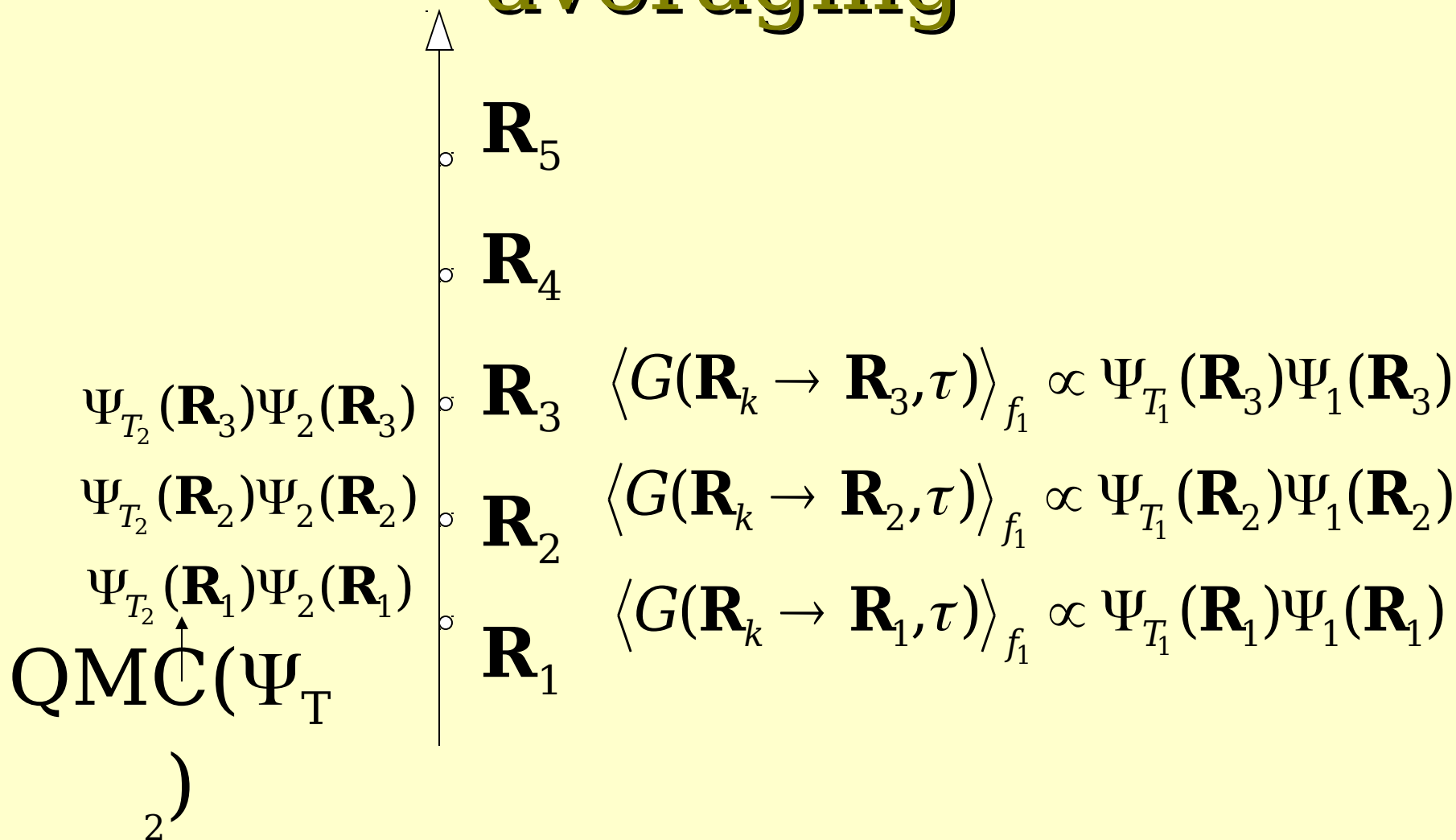
- As before we seek an operator O such that

$$\langle O \rangle_{f_2} \equiv \frac{\langle \Psi_{T_2} | O | \Psi_2 \rangle}{\langle \Psi_{T_2} | \Psi_2 \rangle} = \langle \Psi_1 | A | \Psi_2 \rangle$$

- By inspection

$$O = s_1 s_2 \exp \left[\tau_1 (E_1 - E_{R_1}) \right] \langle G(\mathbf{R}, \tau) \rangle_{f_1} \Psi_{T_1}^{-1}(\mathbf{R}) \Psi_{T_2}^{-1}(\mathbf{R}) A(\mathbf{R})$$

Green's function averaging

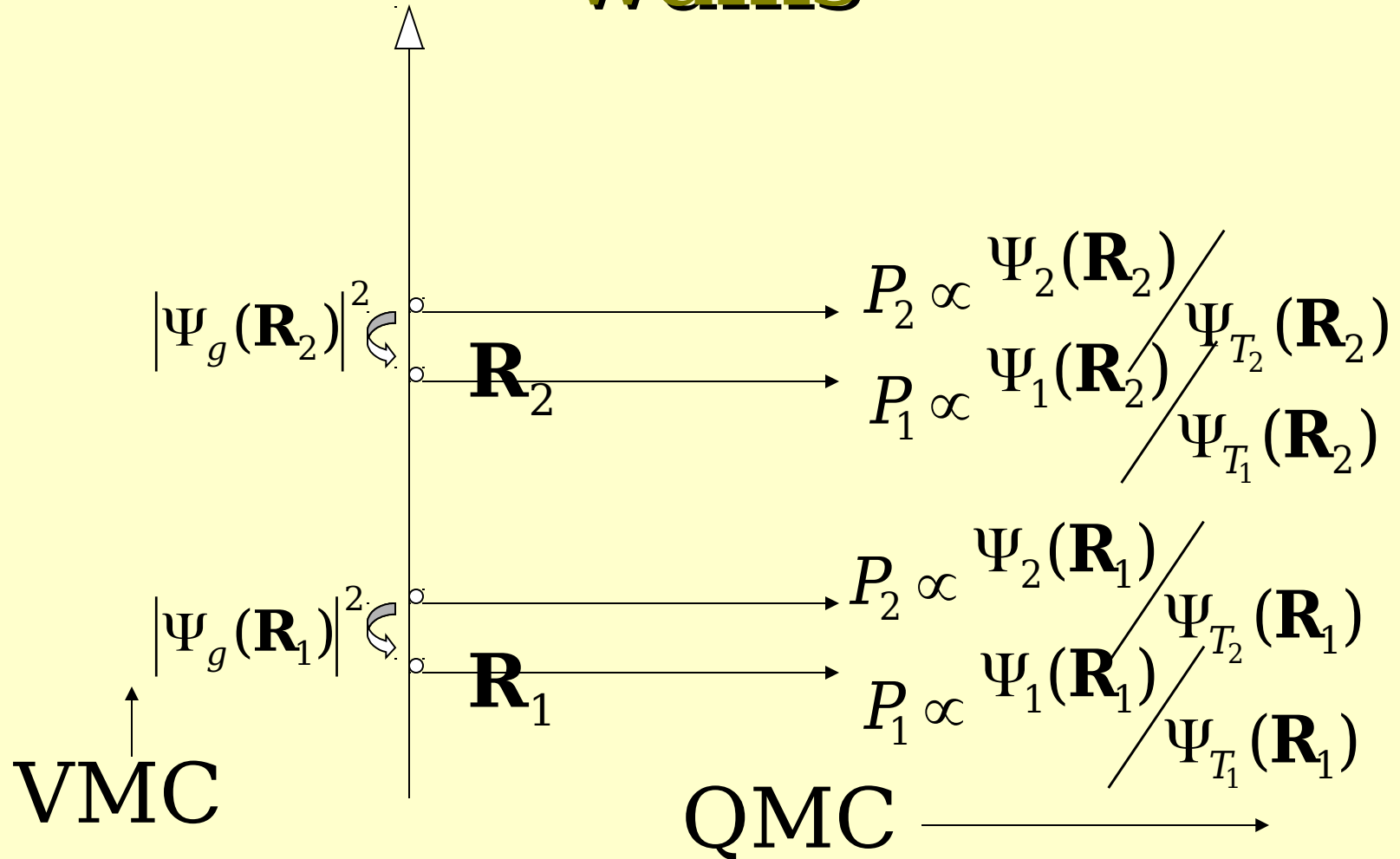


Exact off-diagonal elements

Approaches

- QMC sampling with QMC side walks for weights
 - QMC sampling with Green's function expectation values as weights
 - *VMC sampling with QMC side walks for weights*
-
- R.N. Barnett, P.J. Reynolds, W.A. Lester, Jr., J. Chem. Phys. **96**, 2141 (1992)

VMC walk with QMC side walks



Lessons

- Second order diagonal estimator by combining trial and mixed expectations
- Second order *off-diagonal* requires lots of sampling with reweighting
- Exact algorithms for diagonal elements: reweight by $P(\mathbf{R})$
- Exact algorithms for *off-diagonal* elements: reweight, reweight, ***reweight* !!!**

Algorithms for Computing Matrix Elements by Green's Function Monte Carlo

The End

NATO Advanced Study Institute
on Monte Carlo Methods in
Physics and Chemistry

Cornell University

July 12-25, 1998